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Space-selective valence state manipulation of transition metal ions inside glasses by a femtosecond laser

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We report the observation of space-selective oxidation of Mn^{2+} to Mn^{3+} in a transparent and colorless Mn and Fe ions codoped silicate glass at room temperature by using an 800-nm-femtosecond laser. Difference absorption spectrum of the glass after and before the irradiation of the focused infrared femtosecond pulsed laser showed that a portion of Mn^{2+} ions near the focused part of the laser beam inside the glass were oxidized to Mn^{3+} ions after the laser irradiation. Mn^{3+} ions were stable at the temperatures below 300 °C. It is suggested that Mn^{2+} ions act as hole trapping centers while Fe^{3+} ions as well as active sites in the glass matrix act as electron trapping centers. A promising application was demonstrated for the fabrication of three-dimensional colored image inside a transparent material. © 2001 American Institute of Physics.

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Materials with three dimensionally modulated microstructures has potential applications in optical field.^{1,2} Up to now, there have been much investigation on the three-dimensional microfabrication.^{3–5} Braun and Witzius have successfully fabricated three-dimensional structures of semiconductors by template-directed electrochemical deposition.³ Cumpston *et al.* have succeeded in the fabrication of micro-optical elements with two-photon photopolymerization.⁴ Holographic lithography has been used to fabricate three-dimensional photonic crystals, which have periodical dielectric structures and can manipulate light in much the same way that a superconductor manipulates electrons.⁵

It is well known that laser light can be pulsed and focused to a spot of wavelength order. Ultrashort pulsed laser has been used as a powerful tool to clarify elementary processes, such as excitation-energy relaxation and both electron and proton transfer on nanosecond and picosecond time scales, that occur in a micrometer-sized area.^{6,7} Ultrashort pulsed laser can also be used to make microscopic modifications to transparent materials. The reason for using this laser is that its electric field intensity can reach 100 TW/cm², which is sufficient for inducing nonlinear optical effects in materials by use of a focusing lens, when the pulse width is 100 fs and the pulse energy is 1 μJ. The photoinduced reaction is expected to occur only near the focused part of the laser beam due to nonlinear optical processes.

Up to now, there have been a lot of studies on the microscopic modifications in transparent materials by using

femtosecond lasers.^{8–14} Various induced structures can be produced by using pulsed laser operating at the nonresonant wavelength with pulse widths of the order of femtosecond; colored lines due to the formation of color center, refractive index spot due to densification and defect formation, microvoid due to remelting and shock wave, microcrack due to destructive breakdown, etc.¹⁴ Composite structures were also observed after the focused femtosecond laser irradiation.¹⁴ Promising applications using these phenomena have also been demonstrated for three-dimensional optical memory, integrated optical circuit, and optical display.^{8–14}

In this letter, we report the observation of space selective valence state manipulation of transition metal ions in transparent materials. We observed space selective, persistent photo-oxidation of Mn^{2+} to Mn^{3+} in a silicate glass by focusing 120 fs laser pulses from a regeneratively amplified Ti sapphire laser through a microscope objective lens. Absorption and electron spin resonance spectra were measured for the glass before and after the femtosecond laser irradiation. The mechanism of the phenomenon is also discussed.

Glass composition of the Mn and Fe ions codoped silicate glass sample used in this study was 0.05Fe₂O₃·0.1MnO·70SiO₂·10CaO·20Na₂O(mol %). Reagent grade SiO₂, CaCO₃, Na₂CO₃, Fe₂O₃, and MnO were used as starting materials. An ~40 g batch was mixed, and placed into a platinum crucible. Melting was carried out in an electronic furnace at 1550 °C for 1 h under the ambient atmosphere. Glass sample was obtained by quenching the melt to room temperature. The glass sample thus obtained was transparent and colorless. The glass sample was cut, polished, and subjected to experiments.

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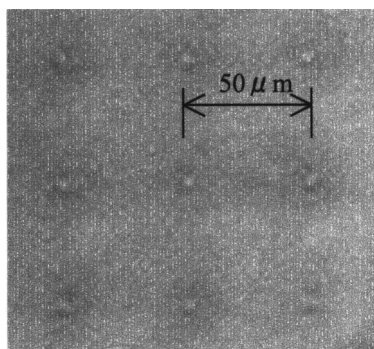


FIG. 1. Image of induced spots in the Mn and Fe ions codoped silicate glass after focused 800 nm femtosecond laser for 1/63 s on each spot. Distance between adjacent spots is 50 μm .

A regeneratively amplified 800-nm-Ti sapphire laser that emits 120 fs, 1 kHz, mode-locked pulses was used for our study. The laser beam with an average power of 400 mW was focused by a 10 \times objective lens with a numerical aperture of 0.30 on the interior of the glass sample with the help of an XYZ stage. The spot size (diameter) of the laser beam was estimated to be 10 μm .

Absorption spectra of the glass samples were measured by a spectrophotometer (JASCO V-570). Electron spin resonance (ESR) measurements were carried out at X-band frequency (9.8 GHz) by an ESR spectrophotometer (JEOL-FE3X). The microwave power, time constant, modulation amplitude, and sweep time was 1 mW, 0.03 s, 1 \times 100, and 4 cm/min, respectively. All of the experiments were carried out at room temperature.

Figure 1 shows the image of the spots after irradiation by the focused infrared femtosecond laser on each spot for 1/63 s (i.e., 16 pulses). A 4 μm spot was formed in the focused area of the laser beam in the Mn and Fe ions codoped glass sample. In addition, a purple colored area with diameter of about 30 μm was observed around the spot. The length of the induced structure along the axis of the laser beam was about 1.5 mm via the observation of optical microscope. To measure the absorption spectrum of the glass sample after the laser irradiation, we wrote a “damaged” plane of 3.0 \times 3.0 mm² inside the glass sample, which consisted of “damaged” lines at an interval of 10 μm by scanning the laser beam at a rate of 1 mm/s. The distance of the plane from the surface of the glass sample was about 0.5 mm.

Figure 2 shows the absorption spectra of the glass

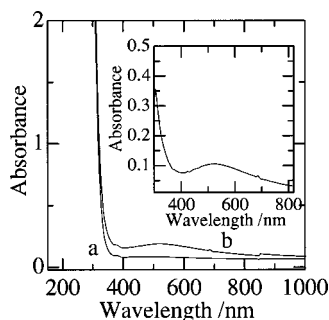


FIG. 2. Absorption spectra of the Mn and Fe ions codoped silicate glass before (a) and after (b) the femtosecond laser irradiation. The inset shows the difference spectrum between absorption of the glass sample after and before the femtosecond laser irradiation.

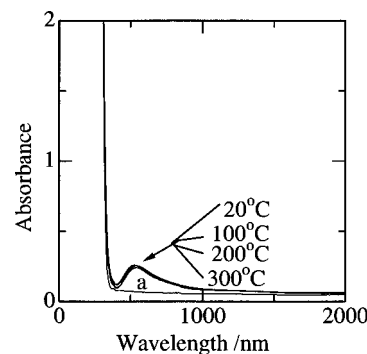


FIG. 3. Absorption spectra of the irradiated Mn and Fe ions codoped silicate glass annealed at various temperatures for 1 h.

sample before (a) and after (b) the femtosecond laser irradiation. No apparent absorption was observed for the unirradiated glass sample in the wavelength region from 400 to 1000 nm, while there was an apparent increase in the absorbance in the wavelength region from 300 to 1000 nm in the irradiated region. The inset of the Fig. 2 shows the difference absorption spectrum of the glass sample after and before the femtosecond laser irradiation. A peak ranging from 400 to 800 nm, peaking at 520 nm was observed. This peak can be ascribed to the absorption of Mn^{3+} ions.^{15,16} In addition, a peak was observed at 320 nm, which can be assigned to the absorption of hole-trapped centers as observed in the x-ray irradiated silicate glasses.¹⁷

Figure 3 shows the absorption spectra of the femtosecond-laser-irradiated glass sample annealed at various temperatures for 1 h. No apparent decrease was observed in the laser-induced absorption at temperature below 300 $^{\circ}\text{C}$. We did not observe any variation for the absorption of the induced Mn^{3+} ions at room temperature even after one month. Therefore, the induced Mn^{3+} ions are thermally stable.

Figure 4 shows the electron spin resonance spectra of the glass sample before and after the femtosecond laser irradiation at room temperature. The spectrum of unirradiated glass exhibits a resolved hyperfine structures of six lines spread over a range of about 500 G in width centered at 3350 G (splitting coefficient $g \sim 2.0$). The spectrum showed a pattern similar to those observed for various glasses containing Mn^{2+} ions.¹⁸ The low resolution of the hyperfine lines is due to the dipolar broadening. In Fig. 1, no apparent absorption due to Mn^{3+} was observed in unirradiated glass. Therefore, most of Mn ions are present as divalent state in glass. Two

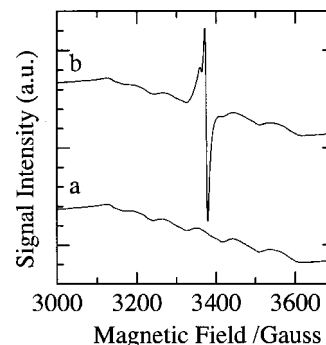


FIG. 4. Electron spin resonance spectra of the Mn and Fe ions codoped silicate glass before (a) and after (b) the femtosecond laser irradiation.

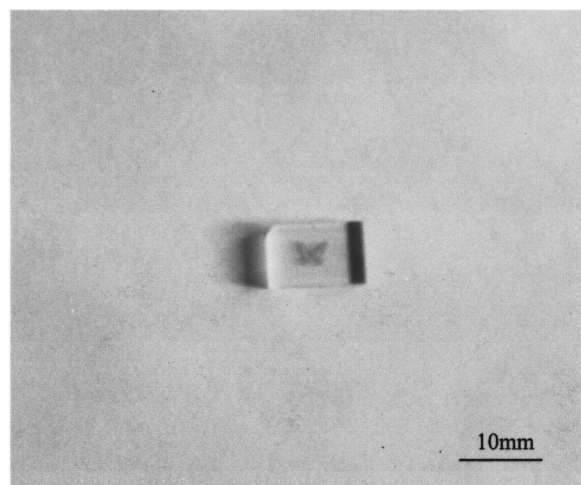


FIG. 5. Image of a butterfly in purple color written inside the glass using the femtosecond laser.

new signals at g of 2.010 and 2.000 were observed in the glass sample after irradiation. The signals can be assigned to hole-trapped centers in the glass matrix.¹⁹

From the above results, a part of Mn^{2+} was oxidized to Mn^{3+} after the femtosecond laser irradiation. Mn and Fe codoped silicate glass sample has no absorption in the wavelength region near 800 nm. Therefore, photo-oxidation of Mn^{2+} to Mn^{3+} should be a nonlinear optical process. We suggest that multiphoton absorption be one of the mechanism of the observed phenomenon.²⁰ Free electrons are generated by the multiphoton absorption of the incident photon and consequent avalanche ionization. Mn^{2+} captures a hole to form Mn^{3+} , while Fe^{3+} as well as active sites in glass matrix may act as electron trapping centers, resulting in the formation of Mn^{3+} . However, the length of the induced structure (1.5 mm) is far longer than that of the Rayleigh length of the focused beam (200 μm). Therefore, other mechanisms also should be taken into consideration. Since the power density is larger than 10^{12} W/cm², nonlinear refractive index largely contributes to the refractive index of the glass during the laser irradiation. The refractive index increases when the intensity of the laser increases and self-focusing of the laser beam occurs. On the other hand, formation of electron plasma due to electric field, causes a decrease in the real part of the refractive index and induces self-defocusing of the beam. The balance between the self-focusing due to the increase of refractive index and self-defocusing due to the plasma formation results in a phenomenon called self-trapping or filamentation.²¹ In the filaments, white light supercontinuum containing Stokes and anti-Stokes wave is generated due to self-phase modulation. The single or two-photon absorption of short wavelength component of the white light supercontinuum causes photoionization of transition ions as well as glass matrix, leading to the formation of Mn^{3+} . We confirmed that the length of the induced structure was directly proportional to the square root of the average power of the laser beam. If we assume that the length of the induced structure is directly proportional to the length of the filament, the result is in good agreement with the theory of Zverev *et al.*²² Therefore, filamentation due to the balance of self-focusing arose from an increase in refrac-

tive index and self-defocusing arose from plasma formation which takes an important role in the oxidation of Mn^{2+} to Mn^{3+} . The trap levels of defect centers may be deep, thus resulting in the stable Mn^{3+} at room temperature. The structural difference among the cross section of the induced structure may result from the high temperature and high pressure at the center part due to the strong plasma formation, and ionization of transition metal ion as well as glass matrix due to the multiphoton absorption of the incident laser and single or two photon absorption of the white light supercontinuum.

In summary, we have observed persistent photo-oxidation of Mn^{2+} to Mn^{3+} in a silicate glass by a focused infrared femtosecond pulsed laser at room temperature. Mn^{2+} is suggested to act as hole trapping centers while Fe^{3+} , active sites in glass matrix act as an electron trapping center. White light supercontinuum takes an important role in the formation of Mn^{3+} . Since the focused area becomes purple after the laser irradiation, it is possible to write a three-dimensional colored image inside the transparent and colorless glass as shown in Fig. 5. Since the length of the induced structure is directly proportional to the square root of the average power of the laser beam, it is possible to control the longitudinal spreading of the oxidation area from several hundred nanometers to several millimeters by selecting the proper irradiation condition. This method should also be useful for the space-selective valence state manipulation of other transition metal ions inside transparent materials. Therefore, the present technique will be useful in the fabrication of three-dimensional colored industrial art object, optical memory, and micro-optical devices.

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